



Review Article

Smart composites — The new era in smart dentistry

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ABSTRACT

The current dental materials were improvised to make them smarter. The use of these smart materials such as, smart ceramics, smart composites, amorphous calcium phosphate releasing pit and fissure sealants, compomers, resin-modified glass ionomer, etc. and other materials such as smart impression material, orthodontic shape memory alloys, smart suture, smart burs, etc. Has revolutionized dentistry. The quest for an ideal restorative material leads to the discovery of a newer generation of materials in dentistry which is called as smart materials. These materials are called smart as they can be altered in a controlled fashion by stimulus such as stress, temperature, pH, moisture, electric or magnetic field. These smart materials hold future in terms of improved efficiency and mark the beginning of a new generation or era in Smart dentistry. The objective of this review article is to review about smart materials and its classification, dental composite resin and its historical background, smart composites, smart monochromatic composite.

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1. Introduction

Composite resin is one of the dental restorative materials which is used routinely in dental clinic as it has great aesthetic, bio compatibility, physical, and mechanical properties. Composite resins are filled resin. They have high compressive strength, abrasion resistance, high translucency and an ease of application.

Composite resin is the mixture of a matrix phase and a reinforcing phase. The reinforcing phase is embedded in a matrix phase. Reinforcing phase or filler is in sheet, fiber or in particle form. The reinforcing phase and matrix phase could be ceramic, metal or polymer^{1,2} Beside the material, the composition of composite resin consists of photo initiator and a coupling agent.^{2,3} Poly methyl methacrylate (PMMA) resin was introduced in late 1940 and in early

1950. The composite resin shrunk severely during the polymerization process. Polymerization shrinkage can lead marginal leakage, high coefficient of thermal expansion, poor wear resistance, and high-water sorption. To overcome this problem, quartz was added to PPMA resin as filler and the purpose of this additional inert filler particle is to form a composite structure.

2. What are Smart Materials?

Smart materials are materials that have properties that may be altered in a controlled fashion by stimuli, such as temperature, stress, moisture, pH, and electric or magnetic fields.⁴ They are called “responsive materials” as they have the inherent capability to sense and react according to changes in the environment.⁵

Smart behaviour generally occurs when a material senses some stimulus from the environment and reacts to it in a useful, reproducible, reliable, and usually in a reversible

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manner. The most important feature of the smart behaviour includes its ability to return to original state even after the stimulus has been removed.⁶ These properties have a beneficial application in a various fields including dentistry also.

Smart materials have been used for a large number of applications. The terms 'intelligent' and 'smart' were first used in the 1980s in the United States to describe materials and systems. The government agencies have developed smart materials who was working on military and aerospace projects but recently their use has been transferred into the civil sector for applications in various areas. The use of the first smart material began with magneto strictive technology, which featured the use of nickel as a sonar source to locate German U-boats by Allied forces during World War I.⁷

The term "smart behaviour" or "smart materials" in the field of dentistry was probably first used in connection with shape memory alloys (SMAs) or Nickel-Titanium (NiTi) alloys, which are used as orthodontic wires. The shape memory effect was first observed by Greniger and Mooradian in copper-zinc and copper-tin alloys in 1938. Nickel-Titanium was developed 50 years ago in the Naval Ordinance Laboratory (NOL) in Silver Springs, Maryland by Buehler et al. In endodontics, 55 wt% Ni and 45 wt% Ti are commonly used, referred to as "55NiTiNOL." NiTi was introduced to endodontics by Walia et al. in 1988.⁸

The smart behavior of GIC was first suggested by Davidson.⁹ It is related with the ability of a gel structure to absorb or release solvent rapidly in response to a stimulus such as temperature, change in pH etc. The number of the pores and its size with the cement can be controlled by the method of mixing conveniently measuring using micro-computed tomography scanning.¹⁰ The smart ionomers mimic the behavior of human dentin. Resin modified glass ionomer cement, giomer or compomer also exhibit these smart characteristics. Example: GC Fuji IX GP EXTRA (Zahnfabrik Bad Säckingen, Germany).

In 1995, the first "all ceramic teeth and bridge" was invented at ETH Zurich based on the process that enables the direct machining of ceramic teeth and bridges. The process involved machining a prefabricated ceramic blank made of zirconia ceramics with a nanocrystalline porous structure in the pre sintered state which is followed by sintering. This invention was introduced in the market by the dental supplier Degudent as CERCON®-Smart Ceramics System.¹¹

Smart prep burs are also called as polymer burs that remove only infected dentin. Smart Burs remove carious dentin by selectively leaving the healthy dentin intact.⁸

Eg: SS White diamond and carbide preparation kit.¹²

SKRTIC created a novel biologically active restorative materials with an aluminium composite panel (ACP) filler which is enclosed in a polymer binder, which may encourage tooth structure regeneration by releasing

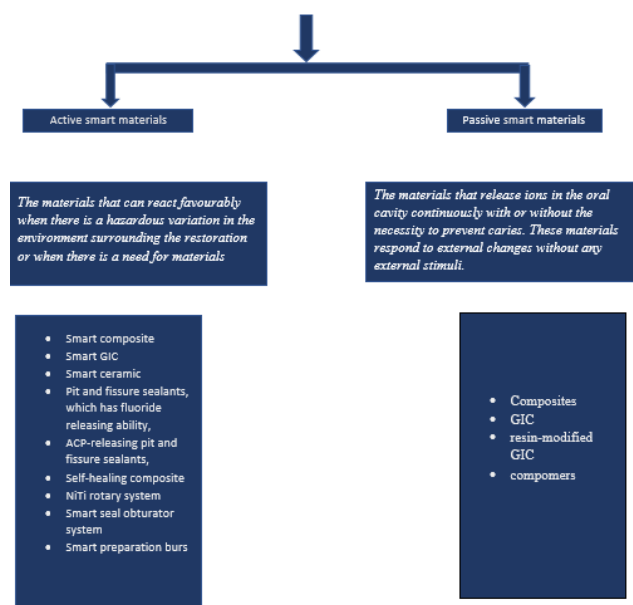
considerable amounts of calcium and phosphate ions over time.¹²

2.1. Requirements of smart material

According to Williams, "Smart" materials can respond to an external stimulus in a specific, controlled way. Conventional filling materials fail because of the formation of secondary caries, fracture of restoration, fracture of tooth, marginal discrepancies, or wear. Materials developed are smart to reduce failures by adding additives to the materials.⁷ Smart materials respond by:

1. Preventing secondary caries
2. Preventing fracture of restoration
3. Preventing fracture of tooth
4. Providing a good marginal integrity
5. Reducing wear
6. Preventing marginal discrepancies
7. Preventing wear¹²

2.2. Classification of smart materials¹²⁻¹⁴



Composite is a three-dimensional compound which consists of two or more chemically dissimilar materials which has excellent properties than those of an individual component. Resin composite presents extremely conservative and provide esthetic restorations to an individual owing to significant progression along with its compatible use for the last couple of decades. Formerly, composites were suggested as a restorative material merely for anterior teeth; however at present, fillers combined with acid etching and its good compatibility to tooth structure have made it worthwhile for anterior as well as posterior restorations.¹⁵ Currently, resin composites are

recommended as an inexpensive and esthetic substitute to other direct and indirect restorations in consequence of its optimization of formulations, up gradation of properties, and innovative methods for application.¹⁶

3. Composite Dentistry Historical Breakthroughs

Dr. Michael Buonocore in the mid 1955 found that phosphoric acid improves the mechanical bonding of the restoration to the acid treated tooth surface.² However; RL Bowen invented dental composites in 1962.¹⁷

In the early 1970s, macrofilled composites were introduced. The leading commercial composite resins were {Concise (3M) and Adaptic (Dentsply Sirona)}. They are composed of large fillers with typical particle sizes ranging from 0 to 5 μm with rough surface texture.¹⁸

In the 1980s, microfilled composites were developed. The commercially popular resin composites were Durafill VS (Kulzer) and Renamel (Cosmedent) with usual particle size ranging from 0.04 to 0.4 μm .¹⁹

In the 1990s, hybrid composites were introduced. As reflected by name, they are composed of organic part which is reinforced by an inorganic phase.²⁰ They were difficult to polish because different sizes of glasses were used in their composition, with particle size of $<2 \mu\text{m}$ and comprise 0.04 μm -sized fumed silica as well.

After the year of 2000, nanofilled and nanohybrid composites were developed as Tetric EvoCeram (Ivoclar Vivadent) and Filtek Supreme Plus (3M) with typical particle size ranging from 5 to 75 nm and nanocluster fillers with particle size ranging from 5 to 20 nm that were less than that of microfilled composites.^{20,21} They exhibited better physical properties similar to the original hybrid resin composite and restorations with a smoother surface texture and polish.²²

By the 2010s, bulk-fill composites were introduced which got approval by many dental practitioners due to less significant polymerization shrinkage with a better depth of cure up to 4 mm.²² The first flowable bulk-fill composite was recognized as SureFil SDR Flow (Dentsply Sirona) that was applied as a base beneath restorations.

In 2018, we have witnessed the launch of other spherical-particle-based composites, notably Harmonize (KaVo Kerr) and Brilliant Everglow (COLTENE). Brilliant Everglow is termed an “all-round” material with dual shade compules, whereas harmonize relies on “crosslinks of spherical silica and zirconia particles together with positive and negative charges.”²³

Also, 2019 brings the introduction of another truly groundbreaking material, Omnicroma (Tokuyama Dental America) (Figure 3). This is the first omnichromatic composite resin-based material that will match any tooth, any shade, on any patient.²³

Flowable bulk-fill materials generally have lower filler loading than nonflowable, sculptable materials and require

that the occlusal layer be filled with a “cap” of a more highly filled composite that is expected to be stronger and more wear resistant under occlusal loading. One example is SureFil SDR flow (Dentsply). According to the manufacturer, this product features, in addition to the lower filler content, a novel UDMA-based monomer with high molecular weight (849 g/mol), which helps to reduce shrinkage.²⁴

Other nonflowable bulk-fill materials include Tetric EvoCeram Bulk-Fill (Ivoclar Vivadent) and Filtek Bulk-Fill (3M-ESPE). Tetric EvoCeram uses a photoinitiator system containing Ivocerin—a germanium-based light initiator, whose greater quantum yield conversion makes it more efficient in promoting polymerization in depth despite the shorter wavelengths needed for its optimal activation.²⁴

Self-adhesive resin composites, such as Vertise Flow and Dyad Flow (Kerr Corporation), have been developed with the goal of simplifying the composite restorative procedure by eliminating its most technique-sensitive step: the adhesive application. The resins in these composites contain glycerol phosphate dimethacrylate, a self-etching, dimethacrylate monomer capable of crosslinking and copolymerization with other methacrylate, as well as the potential for chemical bonding with the tooth’s mineral content.²⁴

The self-adhesive resin-based bulk-fill restorative (classified as self-adhesive composite hybrid by the manufacturer) has been launched under the brand name Surefil one (Dentsply Sirona, Konstanz, Germany). The manufacturer describes the initiator system as a combination of the photoinitiator camphorquinone and a persulfate with two reducing agents both being part of the dark as well as the light curing process. This leads to bulk curing (in the dark) as well as light curing of the surface areas.²⁵

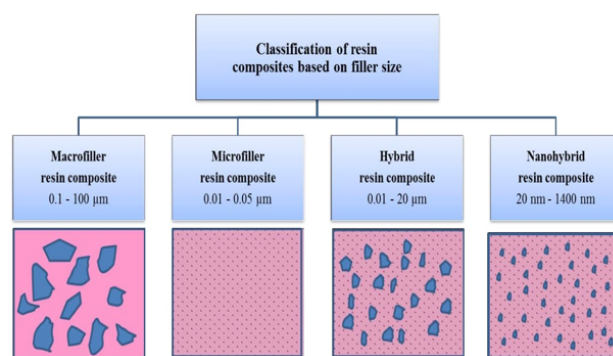


Figure 1: Classification of the composite based on filler size.

4. Smart Composite

Generally, Boskey mentioned that Aaron S. Posner to have firstly described amorphous calcium phosphate (ACP)²⁶ in

the mid-1960s. It was obtained as an amorphous precipitate by accident when mixing high concentrations (30 mM) of calcium chloride and sodium acid phosphate (20 mM) in buffer. ACP based materials have been developed for a number of applications like bases/liners, orthodontic adhesives, endodontic sealers,²⁷ and as pit and fissure sealants.

In bioactive polymeric composites, ACP has been evaluated as a filler phase. Skrtic has developed unique biologically active restorative materials which contains ACP as a filler encapsulated in a polymer binder, that may stimulate the repair of tooth structure because it releases significant amounts of phosphate and calcium ions in a sustained manner. AMORPHOUS CALCIUM PHOSPHATE (ACP) has both preventive and restorative properties, which justify its use in dental cements and adhesives, composites, and pit and fissure sealants.²⁸

4.1. Smart behaviour of composite

The ACP containing composites releases phosphate and calcium ions into saliva milieu, especially in the oral environment caused by bacterial plaque or acidic foods. Then these ions can be deposited as apatitic mineral into tooth structures, which is similar to the hydroxyapatite (HAP) found naturally in teeth and bone. It also has excellent biocompatibility.²⁹ ACP at neutral or high pH remains as ACP. When pH values lowers during a carious attack (at or below 5.8), ACP converts into HAP and precipitates, thus³⁰ replacing the HAP lost to the acid. So, these ions merge within seconds to form a gel when the pH level in the mouth drops below 5.8. In less than 2 minutes, these gel becomes amorphous crystals, resulting in calcium and phosphate ions.³¹ This response of ACP containing composites to the pH can be described as 'smart'. **Ariston pH control:** It is a light-activated alkaline, nano filled glass restorative material. It is introduced by Ivoclar-Vivadent. It releases calcium, hydroxyl ions and fluoride when intraoral pH values drop below the critical pH of 5.5 and counteracts the demineralization of the tooth surface and also aids in remineralisation. This material can be adequately cured in a bulk thickness of up to 4 mm. It is recommended for the restoration of class 1 and class 2 lesions in both permanent and primary teeth.

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2. **Self-repairing or self-healing composite:** This is an epoxy system which contained resin filled microcapsules. If a crack occurs in the epoxy composite material, some of the microcapsules which are destroyed near the crack releases the resin. The resin then subsequently fills the crack and reacts with a Grubbs catalyst dispersed in the epoxy composite, which results in polymerization of the resin and repair of the crack. (Figure 3) Similar systems were demonstrated to have a significantly longer duty cycle under mechanical stress in situ compared to similar systems with the self-repair.^{32–34}

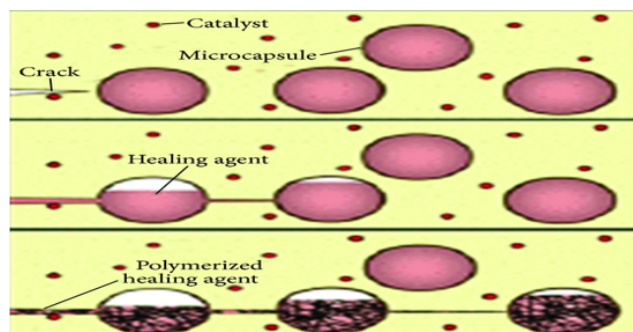


Figure 2: Basic method of the microcapsule approach (Photo courtesy- Google)

4.2. Smart monochromatic composite

Smart monochromatic composite is a leading shade-matching composite that gained more acceptance in recent times. (Figure 3). It possesses distinctive characteristics that are based on “smart chromatic technology.” It has the capability to capture the structural color of its surrounding tooth that is controlled by the size of its filler particles.³⁵ It has no extra dyes or pigments, whereas fillers itself produce red-to-yellow structural color that matches the surrounding tooth color. Color is the light wavelength that enters into our eyes. Human teeth come into the range of red-to-yellow color.³⁵

Smart monochromatic composite is a one-shade material that is specified to match entirely 16 VITA Classical shades (VITA North America, Yorba Linda, CA). It has another shade that is opaque, termed as Blocker to represent the color of dentine in translucent areas like restorations in class IV cavities.

Smart monochromatic composite has a distinctive feature that helps clinicians not be confused by many shades. It presents a rapid and easy method that makes striking and functionally esthetic restorations. Smart monochromatic composite has been recognized to possibly save time in the clinic to get rid of the requirement of shade selection. In this composite, material has homogeneously sized spherical-shaped filler particles. It adjusts the light that is transmitted

all along the red-to-yellow area of the color scale and shows matching the color of neighboring teeth of patients.³⁵

The main characteristics of smart monochromatic composite include better polishing capability, superior flexural and compressive strength, easy handling, clinically satisfactory outcomes, and resistant to ambient light. It carries minimal wear of composite and opposing tooth structure. Smart monochromatic composite is available in the form of opaque-white paste that allows the material more visible to clinicians during manipulation and placement. The material is evenly mixed with adjacent teeth prior to application of light source during curing. A chamfered margin is preferred to get better marginal seal.³⁶



Figure 3: Omnichroma (Photo courtesy- Google)

5. Components of the Smart Monochromatic Composite³⁷

Fillers

Spherical-shaped identical in size supra-nano filler particles (260 nm SiO₂-ZrO₂) that are formed in regular edges. This gave an idea of development for polychromatic composite.

Monomers

UDMA/TEGDMA with filler loading of 79 wt% (68 vol%). UDMA: urethane dimethacrylate and TEGDMA: triethyleneglycol dimethacrylate.

5.1. Recommendations for the smart monochromatic composite

1. Direct restorations in both posterior and anterior teeth.
2. Direct composite veneering.
3. Diastema closure or closure of space between any teeth.
4. Composite and porcelain repair.³⁸

A single shade is only required to match most posterior and anterior teeth. In case of extensive Class III and Class IV restorations, a blocking agent (Omnichroma Blocker (Figure 4) [Tokuyama Dental America]) is used by placing 0.5mm layer before placement of Omnichroma. This masks the inner part of the crown; especially in presence of any

discoloration. The blocker's function is to reduce shade-matching interference.^{18,39}



Figure 4: Omnichroma blocker (Photo courtesy- Google)

In a recent study on OM (Omnichroma), Evans (2020) suggested that the shade difference between the composite (OM) and the tooth decreases as the tooth becomes brighter.⁴⁰ In addition, OM has shown compromised aesthetic outcomes when employed in direct restorations.⁴¹ Therefore, it is critical to ascertain the color matching ability and color stability of OM in comparison to conventional resin-based restorative materials.

5.2. Smart polymer nanocomposites

Polymer nanocomposites (PNCs) are filler-reinforced polymers; in these materials, the filler size is characterized by being of the order of nanometers (< 100 nm) in at least one dimension. Nanofillers can be classified in zero-dimensional (spherical), one-dimensional (layered), and two dimensional (fibrous and tubular), according to the number of dimensions that are outside the nanometric range.⁴²

The integration of different nanofillers to polymeric matrices has been shown to improve mechanical properties and opens up the possibility of creating new materials with a capacity to respond to different chemical, physical, or biological stimuli.⁴³ Different types of nanofillers have been used to obtain nanocomposites, which can be subdivided into two categories according to their ability to respond to stimuli:

1. Inert nanofillers, which lack stimulus-responsive properties and their primary role is the mechanical reinforcement. These nanofillers include silica, cellulose, and clay materials nanoparticles (montmorillonite, hectorite, saponite, laponite, halloysite, etc.^{44–46}
2. Active nanofillers, this type of nanofillers has stimulus-responsive properties, which in addition to reinforcement, provides the stimulus-response capacity to the nanocomposite material.

Examples of this type of material include carbon-based, gold, and magnetic iron oxide nanofillers.^{47,48}

For the synthesis of stimuli-response nanocomposites, active nanofillers are mostly used because these materials can react to different stimuli. As a result, the obtained nanocomposite could respond to electric currents, light, temperature, magnetic field, pH changes, etc.^{49–51} Figure 5.

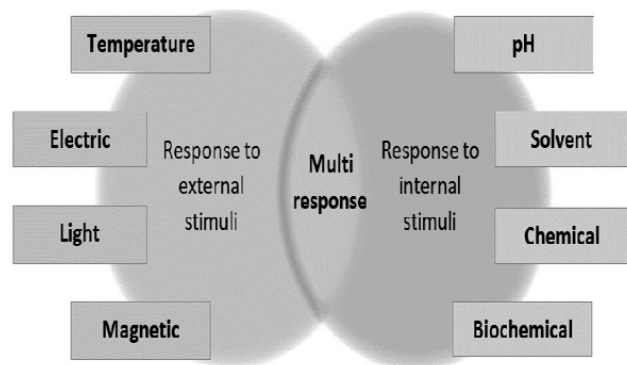


Figure 5: Classification of the responsive nanocomposite (Photo courtesy- Google)

Some commercially available nanocomposites are Filtek Supreme Plus and Filtek Z250 XT (3M ESPE), Premise (Kerr/Sybron), and IPS Empress Direct and Tetric N Ceram (Ivoclar Vivadent).⁵²

6. Conclusion

Science and technology in the 21st century relies heavily on the development of a new materials which are expected to respond to the environmental changes and manifest their own functions according to the optimum conditions. Smart composites are an answer to this requirement and these are environment friendly and responsive materials which alter their properties to perform specific functions. Due to a rapid progress in this area of science and technology, smart composite holds a good promise for the future and in field of Bio Smart. Dentistry. The potential future benefits of smart composite and its structures and systems would prove amazing in their scope. These materials are very useful and time saving and can be used in a very easy manner and handling properties are also good. They also have the ability to sense the environment stimulus. With the passing time, more and more researches are being done in this field. Dental practitioners should be aware of these innovative materials to enable their use and utilize their optimal properties in day-to-day practice to provide quality treatment and it is an effective solution to dental problems. So now, it is the time to think — smart and apply smart materials in dentistry, in our routine clinical practice.

7. Source of Funding

None.

8. Conflict of Interest

None.

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